

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### The Production of Manganese Hydroxide

We, THE GEIGY COMPANY LIMITED, a British company, whose registered office is at 15, Norfolk Street, Manchester, 2, Lancashire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of manganese hydroxide from liquors containing manganous salts. Such liquors are produced as by-products from oxidations with manganese compounds in which the manganese is in a higher state of oxidation than manganous, e.g. manganese dioxide, manganic oxide, manganic salts or manganates or permanganates. These liquors contain impurities which it is frequently difficult to remove. Accordingly such liquors are frequently either treated as waste or are treated to recover manganese compounds in a crude impure form. It is an object of the invention to prepare from such by-product liquors manganous hydroxide in a very pure form.

A typical instance of the production of liquors containing manganous salts by a process involving the oxidation of an organic compound is that in which manganese dioxide ore is used with sulphuric acid to oxidise aniline to benzoquinone. The resulting liquors after separation of the benzoquinone contain manganous sulphate, sulphuric acid, aniline sulphate, ammonium sulphate, and alkaline earth metal sulphates derived from the original manganese dioxide ore together with other impurities derived from the original ore and from the plant, and are highly acidic in character. After neutralisation of the greater part of the excess acid with lime, they contain additional quantities of calcium sulphate. Most of the heavy metal salt impurities are relatively unimportant since they either precipitate on neutralisation of the excess acid or are held up in solution by the ammonium sulphate. By rendering the solution alkaline the manganese

may be precipitated as manganous hydroxide, but alkali metal or alkaline earth metal compounds are liable to contaminate the precipitate.

The present invention is based on the discovery that if the liquor after neutralisation of the excess acid is treated with an oxide or hydroxide as hereinafter specified at a pH value not exceeding 9 and in the presence of an ammonium salt to precipitate manganous hydroxide, the precipitated manganous hydroxide is substantially free from alkali metal and alkaline earth metal compounds even if such compounds were used for the precipitation.

The oxide or hydroxide used for the precipitation must be one which does not form an insoluble salt with the acid radicals present in the reaction mixture and which when dissolved or stirred with water is capable of imparting a pH value of at least 10 thereto. For practical purposes such oxides or hydroxides are those of the alkali or alkaline earth metals or of ammonium or organic bases or of magnesium. Obviously if the acid radicals present are sulphates the use of an alkaline earth metal hydroxide is not permissible whereas if the sulphate radical is substantially absent and the acid radicals present are chlorides any of the hydroxides specified above may be used.

According to the present invention there is provided a process for recovering manganese as manganous hydroxide from aqueous liquors containing in solution manganous salts, comprising the steps of bringing the pH of the liquid to a value between 8 and 8.5, separating from the liquor any impurities precipitated at that value, adding to the liquor in the presence of ammonium salt a basic oxide or hydroxide which when mixed with water is capable of imparting a pH value of at least 10 thereto and which does not form a water-insoluble salt with any acid radical present in the liquor, said compound being added in such restricted quantity that the pH value is increased to a value not greater than 9, whereby to cause

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manganous hydroxide to precipitate without substantial co-precipitation of any compound of any other metal present in solution, and separating said precipitated manganous hydroxide.

By operating in accordance with the invention it is possible to remove by precipitation as manganous hydroxide up to 85% of the manganese present in the liquor and the precipitated manganous hydroxide is found to contain more than 0.03% of calcium or other alkaline earth metals and not more than 0.01% of sodium if caustic soda were used as the precipitant. This is surprising because calcium and sodium are adsorbed on precipitated manganous hydroxide if the pH value of the liquid precipitation medium is permitted to rise above 9.

In carrying the invention into effect starting from a liquor containing one or more ammonium compounds such as a sulphate, it is convenient first to neutralise the greater part of excess acid with lime to a pH value of about 4. At this stage the liquor is filtered so that any iron present is removed as ferric oxide or hydroxide and any calcium sulphate formed during the neutralisation is also removed. The oxide or hydroxide used for the precipitation is then added until a pH value within the range 8 to 8.5 is established when the liquor is again filtered. This removes any other metal compounds precipitated before the manganese. If the liquor contains less than 50 g./l. of manganese it is convenient to effect the second filtration at a pH value of 8.5 since the separated precipitate will contain substantially no manganese but will consist almost entirely of precipitated impurities. If, however, the liquor contains more than 50 g./l. manganese compounds it is preferable to effect such second filtration at a value not exceeding pH 8. The preliminary filtration at about pH 4 is not essential but it is desirable since it assists recovery of the precipitated impurities in that it separates the bulk of the iron and calcium sulphate from the remaining impurities which are not precipitated at about pH 4.

The precipitating oxide or hydroxide is then added in such quantities that the pH value of the liquor never rises above 9 whereby the precipitate formed consists of manganous hydroxide of the purity stated above.

The residual liquor which contains 15% of the manganese originally present may be further worked up by precipitating the manganese preferably as the carbonate by means of a water-soluble carbonate and returning the precipitated carbonate to a fresh batch of the original liquor for treatment in accordance with the invention.

If the original liquor is devoid of ammonium compounds ammonia or ammonium salts must be introduced at some stage prior to the precipitation of the manganese. Such addition

may be very small and need not exceed an amount necessary to make a 1% concentration of ammonia in the liquor. Larger quantities may be added without disadvantage. Such addition is preferably only effected after the filtration at a pH within the range 8.0 to 8.5 and may be effected by direct addition of an ammonium salt prior to the precipitation of the manganese, and after the filtration referred to above or by using ammonium hydroxide as precipitating oxide or hydroxide after such filtration.

The invention is further illustrated in the following examples:—

#### EXAMPLE 1.

This example illustrates the process applied to a manganese liquor containing more than 50 g./l. of manganese.

A manganous sulphate liquor obtained from the manufacture of hydroquinone contained the following principal inorganic components:—

	Grams per litre
Manganous sulphate ( $\text{MnSO}_4$ )	186
(Manganese (Mn) - - - - -)	68.4)
Ammonium sulphate ( $(\text{NH}_4)_2\text{SO}_4$ )	33
Sulphuric acid - - - - -	98
Suspended matter - - - - -	1.3

Dry free flowing lime powder (92.5%  $\text{Ca(OH)}_2$ ) was fed slowly into 1000 litres of vigorously stirred liquor until the pH value rose to 8. The lime neutralised the free sulphuric acid and separated as calcium sulphate. It also precipitated other matter insoluble in liquor of pH value 8. About 80 kgs. of the lime were required, and the addition occupied about one hour. Stirring was continued for a further half hour, and the mixture then left to stand overnight to complete the separation of calcium sulphate. The mixture was stirred again to form an even suspension of the precipitated matter, largely calcium sulphate, and the slurry produced pumped into a filter press. The filter cake was washed with a small volume of water. The combined clear liquor and washings amounted to about 1060 litres, and had the following concentrations of principal components:—

	Grams per litre
Manganous sulphate - - - - -	174
Ammonium sulphate - - - - -	31

The above liquor was transferred to a mixing vessel equipped with a high speed stirrer. Caustic soda solution containing 200 grams per litre of 96% NaOH was run into the vigorously stirred liquor until the pH value rose to 9, to precipitate manganese as manganous hydroxide, care being taken to avoid high local concentrations of alkali. About 430 litres of the alkali were required and the addition occupied about an hour. Stirring was continued for about another half hour and the mixture passed to a filter press to recover the manganese hydroxide.

oxide. The cake of product was washed in the press until the washings were free from sulphate, then dried in an oven at about 110° C. to a friable powder. The yield was 104 kgs. of product having the following percentage composition:—

	Manganese (Mn) - - -	54.9%
	Silica, as SiO <sub>2</sub> - - -	0.04%
	Calcium, as CaO - - -	0.02%
10	Sodium, as Na <sub>2</sub> O - - -	0.01%

The remainder of the product was substantially water. The manganese recovered in the product amounted to 84% of the manganese in the original liquor.

#### 15 EXAMPLE 2.

This example illustrates the application of the process to a liquor containing less than 50 g./l. of manganese, and free from ammonium salts, obtained from a ferrous chloride solution by treatment with manganic oxide. This liquor contained the following principal components:—

	Grams per litre
25	Manganous chloride (MnCl <sub>2</sub> ) - - - 76
	(Manganese (Mn) - - - 33)
	Ferric chloride (FeCl <sub>3</sub> ) - - - 8
	Hydrochloric acid (HCl) - - - 5.5
	Suspended matter - - - 1.2

The ferric chloride resulted from incidental oxidation of some of the ferrous chloride and the hydrochloric acid resulted from hydrolysis of some of the ferric chloride. 100 litres of this solution were vigorously stirred and then carefully treated with a caustic soda solution containing 100 grams of 96% NaOH per litre until the pH value rose to 8.5, to neutralise the free acid and precipitate the iron as hydroxide. Other matter precipitable at that pH value naturally separated also. About 12.5 litres of the caustic soda solution were required. The solution after stirring for another 20 minutes was allowed to settle overnight and then decanted through a filter. 4 kgs. of solid ammonia chloride were dissolved in the clear filtrate, which measured approximately 105 litres. The solution was again vigorously stirred and manganese precipitated as manganous hydroxide by the slow addition of more of the caustic soda solution until the pH value of the liquor rose to 9. About 40 litres of the caustic soda solution were needed, and were added over a period of about 15 minutes. Stirring was continued for about another 15 minutes and the mixture then filtered on a filter press. The cake of manganese hydroxide was washed in the press until free from chloride, and then dried in an oven at about 110° C to a friable powder. 5 kgs. of product were obtained having the following percentage composition:—

60	Manganese (Mn) - - -	52.4%
	Silica, as SiO <sub>2</sub> - - -	0.03%
	Calcium, as CaO - - -	0.01%
	Sodium, as Na <sub>2</sub> O - - -	0.01

The remainder of the product was substantially water. The manganese recovered in the product amounted to about 80% of the manganese in the original liquor.

In the above example hydrated lime may be used in place of the caustic soda, but the process is slower owing to the care needed to ensure that an excess quantity is not added at each stage, and that no undissolved lime remains in the product in the final stage.

#### WHAT WE CLAIM IS:—

1. A process for recovering manganese as manganous hydroxide from aqueous liquors containing in solution manganous salts, comprising the steps of bringing the pH of the liquid to a value between 8 and 8.5, separating from the liquor any impurities precipitated at that value, adding to the liquor in the presence of ammonium salt a basic oxide or hydroxide which when mixed with water is capable of imparting a pH value of at least 10 thereto and which does not form a water-insoluble salt with any acid radical present in the liquor, said compound being added in such restricted quantity that the pH value is increased to a value not greater than 9, whereby to cause manganous hydroxide to precipitate without substantial co-precipitation of any compound of any other metal present in solution, and separating said precipitated manganous hydroxide.

2. A process as claimed in Claim 1, in which the starting material is an acid aqueous liquor and the process comprises increasing the pH value in stages and filtering at the end of each stage, the first stage consisting in adjusting the pH of the liquor to a value of 4 followed by filtering off any precipitated impurities, the second stage consisting in adjusting the pH of the liquor to a value of between 8 and 8.5 followed by filtering off any precipitated impurities and the third stage consisting in treatment of the liquor in presence of ammonium salt with a basic oxide or hydroxide as specified in Claim 1, and subsequent filtration of manganous hydroxide at a pH value not greater than 9.

3. A process as claimed in Claim 1 or 2, in which the starting material is an aqueous liquor containing in solution more than 50 g./l. of manganous salt calculated as manganese and the pH adjustment which precedes the treatment to precipitate manganous hydroxide consists in bringing the pH to a value of 8.

4. A process as claimed in Claim 1 or 2, in which the starting material is an aqueous liquor containing in solution less than 50 g./l. of manganous salt calculated as manganese and the adjustment of the pH which precedes the treatment to precipitate manganous hydroxide consists in bringing the pH of the liquor to a value of 8.5.

5. A process as claimed in any preceding claim, in which the mother liquor remaining

after the separation of manganous hydroxide precipitated at a pH not greater than 9 is treated with a water-soluble carbonate to precipitate residual manganese as the carbonate and the resulting precipitated carbonate is added to a fresh batch of liquor for treatment in accordance with Claim 1.

6. A process for recovering manganese as manganous hydroxide from liquors containing

manganous salts, substantially as described in either of the examples.

7. Manganous hydroxide, whenever produced by a process as claimed in any of Claims 1 to 6.

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#### PROVISIONAL SPECIFICATION

#### The Production of Manganese Hydroxide

15 We, THE GEIGY COMPANY LIMITED, a British company, whose registered office is at 15, Norfolk Street, Manchester, 2, Lancashire, do hereby declare this invention to be described in the following statement:—

20 This invention relates to the production of manganese hydroxide from liquors containing manganese salts. Such liquors are produced as by-products from oxidations with manganese compounds in which the manganese is in a higher state of oxidation than manganous, e.g. manganese dioxide, manganic oxide, manganic salts or manganates or permanganates. These liquors contain impurities which it is frequently difficult to remove. Accordingly such liquors are frequently either treated as waste or are treated to recover manganese compounds in a crude impure form. It is an object of the invention to prepare from such by-product liquors manganous hydroxide in a very pure form.

35 A typical instance of the production of liquors containing manganese salts by a process involving the oxidation of an organic compound is that in which manganese dioxide is used to oxidise aniline to benzoquinone. The resulting liquors after separation of the benzoquinone contain manganese sulphate, sulphuric acid, aniline sulphate, ammonium sulphate and alkaline earth metal sulphates derived from the original manganese dioxide ore together with other impurities derived from the original ore and from the plant, and are highly acidic in character. After neutralisation of the greater part of the excess acid with lime, they contain additional quantities of calcium sulphate. Most of the heavy metal salt impurities are relatively unimportant since they either precipitate on neutralisation of the excess acid or are held up in solution by the ammonium sulphate. By rendering the solution alkaline the manganese may be precipitated as the hydroxide, but alkali metal or alkaline earth metal compounds are liable to contaminate the precipitate.

60 The present invention is based on the discovery that if the liquor after neutralisation of the excess acid is treated with an oxide or hydroxide as hereinafter specified at a pH value not exceeding 9 and in the presence of an ammonium compound to precipitate man-

ganese hydroxide, the precipitated manganese hydroxide is substantially free from alkali metal and alkaline earth metal compounds even if such compounds were used for the precipitation.

70 The oxide or hydroxide used for the precipitation must be one which does not form an insoluble salt with the acid radicals present in the reaction mixture and which when dissolved or stirred with water is capable of imparting a pH value of at least 10 to the aqueous medium. For practical purposes such oxides or hydroxides are those of the alkali or alkaline earth metals or of ammonium or organic bases or of magnesium. Obviously if the acid radicals present are sulphates the use of an alkaline earth metal hydroxide is not permissible whereas if the sulphate radical is substantially absent and the acid radicals present are chlorides any of the hydroxides specified above may be used.

85 By operating in accordance with the invention it is possible to remove by precipitation as hydroxide up to 85% of the manganese present in the liquor and the precipitated manganese hydroxide is found to contain not more than 0.03% of calcium or other alkaline earth metals and not more than 0.01% of sodium if caustic soda was used as the precipitant. This is surprising because calcium and sodium are adsorbed on precipitated manganese hydroxide if the pH value of the liquid precipitation medium is permitted to rise above 9.0.

100 In carrying the invention into effect starting from a liquor containing one or more ammonium compounds such as a sulphate, it is convenient first to neutralise the greater part of excess acid with lime to a pH value of about 4.0. At this stage the liquor is filtered so that any iron present is removed as ferric oxide or hydroxide and any calcium sulphate formed during the neutralisation is also removed. The oxide or hydroxide used for the precipitation is then added until a pH value within the range 8.0 to 8.5 is established when the liquor is again filtered. This removes any other metal compounds precipitated before the manganese. If the liquor contains less than 5% of manganese it is convenient to effect the second filtration at a pH value of 8.5 since the separated precipitate will contain substantially no

5 manganese but will consist almost entirely of precipitated impurities. If however, the liquor contains more than 5% manganese compounds it is preferable to effect such second filtration at a value not exceeding pH 8.0. The preliminary filtration at about pH 4.0 is not essential but it is desirable since it assists recovery of the precipitated impurities in that it separates the bulk of the iron and calcium sulphate from the remaining impurities which are not precipitated at about pH 4.0.

10 The precipitating oxide or hydroxide is then added in such quantities that the pH value of the liquor never rises above 9.0 and the precipitate formed consists of manganese hydroxide of the purity stated above.

15 The residual liquor which contains 15% of the manganese originally present may be further worked up by precipitating the manganese preferably as the carbonate and returning the precipitated carbonate to a fresh batch of the original liquor for treatment in accordance with the invention.

If the original liquor is devoid of ammonium compounds ammonia or ammonium salts must be introduced at some stage prior to the precipitation of the manganese. Such addition may be very small and need not exceed an amount, necessary to make a 1% concentration of ammonia in the liquor. Larger quantities may be added without disadvantage. Such addition is preferably only effected after the filtration at a pH within the range 8.0 to 8.5 and may be effected by direct addition of an ammonium salt prior to the precipitation of the manganese, and after the filtration referred to above or by using ammonium hydroxide as the precipitating oxide or hydroxide after such filtration.

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